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Behavior of Slow Electrons in Polar Crystals

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BEHAVIOR OF SLOW ELECTRONS IN POLAR CRYSTALS

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Abstract: The effective mass of slow electrons in polar crystals is investigated using the continuum model of Pekar and Fröhlich, Pelzer and Zienau. The Hamiltonian is studied in a Fock representation so that effects of several quanta can be assessed. The calculations show that the effective mass is larger than that predicted by the one quantum solution, but that the effective mass is still small for weakly polar crystals. For excess electrons in strongly polar crystals many quantum contributions must be included and the present method is inappropriate. It is uncertain whether the effective mass is small in this case. Holes in polar crystals appear to satisfy the conditions for the validity of the theory of Landau and Pekar which predicts a high effective mass.

1. Introduction

The behavior of excess slow electrons in polar crystals has been a subject of controversy and confusion from the theoretical point of view for some time. Landau¹⁾ and independently von Hippel²⁾ have proposed the idea that an electron can be self-trapped because a slow electron displaces the ions about it which, in turn, create a field that prevents the electron from escaping. This possibility has been discussed by Mott and Gurney³⁾ and led

1) L. Landau, Phys. Zt. Sowjet 3, 664 (1933).

2) A. von Hippel, Z. Physik 101, 680 (1936); J. Chem. Phys. 8, 605 (1940).

3) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Oxford Press, 1st ed. p. 86.

to the expectation that a slow electron introduced into the conduction band should be trapped after some time and should occupy a discrete level. One should observe optical absorption lines corresponding to the raising of such a trapped electron into excited discrete levels or into a continuum. In fact, the trapped electrons were identified with the F centers studied by Pohl and collaborators until indirect arguments removed this possibility (p. 113 of Ref. 3). The optical absorption lines should be found experimentally for all polar crystals provided enough self-trapped electrons can be obtained, i.e., if enough excess electrons can be injected into the crystal, and provided other trapping processes do not have overwhelmingly greater cross sections. Experimentally, these lines do not seem to have been found.^{3, 4)}

In addition to the optical behavior it was expected that slow electrons (or slow holes) would show very low mobilities at low temperatures. It was thought that it would be necessary for the ions to assume new configurations in order that the electron be able to move and that at low temperatures this would be improbable. This would imply strongly temperature-dependent mobilities. From the experimental point of view the very great effect of trapping by defects makes it difficult to obtain information about self-trapped electrons by mobility measurements.

The preceding two examples indicate that self-trapping would have serious consequences for the behavior of slow electrons in polar crystals. In addition to the cases mentioned we might expect an influence on prebreakdown currents, breakdown strengths, cross sections for capture by defects, temperature shift of bands, motion of holes, etc.

The present work was undertaken because of a serious challenge to the ideas outlined above. Fröhlich, Pelzer, and Zienau⁵⁾ presented a quantum-

4) W.H.Duerig, Phys. Rev. 86, 565 (1952).

5) H.Fröhlich, H.Pelzer, S.Zienau, Phil. Mag. 41, 221 (1950). This work will subsequently be referred to as F.P.Z.

mechanical treatment of the interaction of an electron and the polar optical modes of vibration using a model which is a good representation of the actual situation in polar crystals. They concluded that self-trapping does not exist, and that electrons can move freely throughout polar crystals with an effective mass close to that of a free, excess, conduction electron. The discrete optical levels do not exist according to this treatment and, since the lattice polarization is only weakly coupled to the electron, the continuous absorption by free electrons should be computable by perturbation-type methods.

Somewhat earlier, work by Landau and Pekar⁶⁾ and Pekar⁷⁾ also showed that electrons can move through polar crystals. However, their calculations led to high effective masses which could be of the order of hundreds of electron masses for the alkali halides, in flat contradiction to the F.P.Z. contention. This disagreement is particularly interesting since both sets of investigators start from the same Hamiltonian but use different methods of solution. In the Landau and Pekar work discrete optical transitions cannot occur, but the strong coupling with the lattice should lead to important modifications of the continuous absorption of light by the electron.

In order to clarify the reasons for the discrepancy mentioned and to find correct values for the effective mass, we have used a method which contains the F.P.Z. treatment as the first stage but remains valid for stronger interaction. Accounts of this method, as well as preliminary estimates, were presented at the Tufts meeting of the American Physical Society⁸⁾ and in Progress Report XI of the Laboratory for Insulation Research.⁹⁾ The method takes advantage of the fact that the lattice quanta form a system of Bosons

6) L.D.Landau and S.Pekar, Zh. Exp. Theor. Phys. 18, 419 (1948).

7) S.Pekar, Zh. Exp. Theor. Phys. 19, 796 (1949).

8) E.P.Gross, Bull. Amer. Phys. Soc., Tufts Meeting, May 24, 1952; Phys. Rev. 88, 153 (1952).

9) Progress Report XI, Laboratory for Insulation Research, May, 1952.

with symmetric wave functions; one works in a series of configuration spaces in a way first introduced by Fock¹⁰⁾ and used by Tomonaga¹¹⁾ in his intermediate coupling meson theory. The method of approximation used has been developed by Schweber¹²⁾ in a thesis on the configuration space treatment of relativistic field theories. It is based on a systematic development according to the number of quanta present in the wave function.

For further discussion it is convenient to introduce the dimensionless quantity

$$\alpha = e^2 \left(\frac{m_c}{2 \hbar^3 \omega} \right)^{1/2} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right)$$

which measures the strength of interaction between the electron and the optical polar modes. Here n is the optical index of refraction, ϵ is the static dielectric constant, m_c is the mass of the electron in the conduction zone and ω is the angular frequency of long wavelength longitudinal optical modes. Values of α are somewhat uncertain, chiefly because one does not have data on m_c . However, for typical polar crystals values of α are: TlBr, 2.5 to 4.5; AgCl, 3.0 to 5.5; KBr, 5.0 to 8.0.

The first figure refers to $m_c \simeq 0.7$ electron masses, the second to $m_c \simeq 2.0$. We will show in this report that the treatment of F.P.Z. gives correct results for the energy and effective mass when $\alpha < 0.5$. For values of α up to 2 it is adequate to include two quantum terms in the wave function while for $\alpha > 3$ inclusion of at least three quantum terms is needed and a treatment according to the number of quanta present may be inappropriate. Most of the calculations are carried for a one-dimensional case which is closely related to the real case. For $\alpha < 2$ a linear dependence of the lowest energy state and the effective mass on α appears to fit the numerical results approxi-

10) V. Fock, Z. Physik 75, 622(1932).

11) S. Tomonaga, Prog. Theor. Phys. 2, 6 (1947).

12) S. Schweber, Thesis, Princeton (1952); Phys. Rev. 84, 1259 (1951).

mately, while for large α it appears that, if higher quantum terms were included in the wave function, both energy and effective mass would vary more rapidly with α . This is relevant to the discussion of other treatments which will now be undertaken.

Several important new attacks on the electron-lattice problem have appeared in recent months. We shall try to summarize the situation as it appears at the present time. Lee and Pines¹³⁾ have set up the problem, in Fock space, as we have done, but have made use of a variational method, in the spirit of the Tomonaga intermediate coupling theory.^{11, 14)} The trial wave functions are products of functions for each wave vector so that correlations between successive quantum emissions are neglected. They find for the effective mass $m^* = m_c(1 + \alpha/6)$ and for the energy depression of the lowest state $E = -\alpha\hbar\omega$. The mean number of quanta present is found to be $\alpha/2$. These results agree with our treatment for $\alpha < 3$, where we are able to carry out the calculations, so that good results are obtained for energy and effective mass in spite of the poor wave functions. In addition, the mathematical simplification is considerable, making the method very useful. If one inserts typical values for α one sees that for almost all cases $m^* < 2m_c$. These effective masses are larger than those of F.P.Z., but are still small and would bear out their contention at least as far as the effective mass problem is concerned. Another type of treatment, valid for weak interactions has been presented by Tyablikov.^{15, 16)} He finds $m^* = m_c/(1 - \alpha/6)$ and $E = -\alpha\hbar\omega$, agreeing with the intermediate coupling result to the first power of α . These results, however,

13) T.D. Lee and D. Pines, Private communication, to be published.

14) Cf. P. T. Matthews, and A. Salam, Phys. Rev. 86, 715 (1952).

15) S. V. Tyablikov, Z. Exp. Theor. Physics 21, 16 (1951).

16) S. V. Tyablikov, Z. Exp. Theor. Physics 22, 513 (1952).

must break down for larger α . Pekar,⁷⁾ using the variational method, finds a trial function yielding $E = -0.1 \alpha^2 \hbar \omega$. This will be discussed further in Section 2 but for the present we note that for large α this energy is lower than that given by the intermediate and weak coupling approaches. The detailed numerical calculations of this report indicate that the linear law begins to break down for $\alpha > 3$.

Bogoliubov¹⁷⁾ and Tyablikov,^{16, 18)} have developed a new, adiabatic method for treating the electron-lattice interaction which is valid for $\alpha \gg 1$. The results are $E = -0.1 \alpha^2 \hbar \omega$ and $m^* = 27(\alpha/b)^4 m_c$, in close agreement with Landau and Pekar⁶⁾ and providing a quantummechanical justification of the semiclassical work of these authors. If one compares the energy depressions of the intermediate coupling with those of the adiabatic method one sees that only for couplings stronger than $\alpha \simeq 10$ does the adiabatic method give lower energies. At this value the two theories predict $m^* \simeq 2.7 m_c$ and $m^* \simeq 210 m_c$, respectively.[†] For these strong interactions the assumption of uncorrelated quantum emissions breaks down and intermediate coupling theory leads to wrong values for the effective mass. Since the effective masses do not match at $\alpha = 10$, it is difficult to give precise values for α somewhat less than 10. The numerical calculations indicate that both intermediate coupling and a treatment based on a small number of quanta with correct wave functions begins to break down for $\alpha > 3$, so that at $\alpha = 6$ the result is intermediate between $m^* = 27 m_c$ predicted by adiabatic theory and $m^* \simeq 2 m_c$ predicted by other treatments. Thus for strongly polar crystals the situation is still somewhat uncertain. For the lower values of α characteristic of the silver

17) N. N. Bogoliubov, Ukr. Mat. Zhurnal 2, 3 (1950).

18) S. V. Tyablikov, Zh. Exp. Theor. Phys. 21, 377 (1951).

[†] The figure $m^* = 432$ electron masses for NaCl given in reference 6 appears to be based on a use of m_c between 2 and 3.

and thalious halides all the theories predict $m^* \approx 2m_c$ in spite of the fact that the adiabatic approximation is no longer valid. For positive holes in the "valence" band the high masses m_c would lead to large values of α and thus to extremely large effective masses.

One is interested in asking whether any of the theoretical results in question can be checked experimentally. For the alkali halides, where the coupling is greatest and the effective mass highest, it seems very difficult to determine the effects of lattice polarization either by optical measurements on free carriers or by mobility measurements since the large number of traps and defects prevent the attainment of an appreciable concentration of electrons in the conduction zones. The experimental situation appears to be more hopeful in less polar crystals such as the silver halides where mobility measurements by Haynes and Shockley¹⁹⁾ and Smith et al.²⁰⁾ have shown that electrons can be moved across an entire single crystal without being trapped. Measurements of the absolute value of the mobility and its temperature dependence would be particularly important.[†] A high effective mass should be measurable at a low temperature. The optical modes are frozen out and the chief determinants of the Hall mobility will be a mean time of collision determined by scattering by acoustic modes, impurity and defect scattering, and the effective mass determined primarily by interaction with the polar modes. However, if present theory is correct, $m^* \approx 2m_c$ which is too small an effect to overcome the crudity of the present state of theory as regards a calculation of the mean collision time.

19) J.R.Haynes and W.Shockley, Phys. Rev. 82, 935 (1951).

20) L.P.Smith, "Semi-Conducting Materials," ed. H.Henisch, London, Butterworth, Ltd., 1951, p.114.

† Hofstadter²¹⁾ gives values at 77°K for AgCl, 1570 cm²/volt sec.; AgBr, 296 cm²/volt sec.; TlBr, 880 cm²/volt sec.

21) R.Hofstadter, Nucleonics 4, 9 (1949).

The experiments of Haynes and Shockley¹⁹⁾ on AgCl and Engelhard on Cu_2O ²²⁾ refer to higher temperatures where scattering by the optical modes dominates. These experiments have been analyzed using the Fröhlich-Mott²³⁾ theory which is a perturbation treatment. This means that the treatment does not even correspond in accuracy to the F.P.Z. calculation of the effective mass; thus a better method is needed. It is possible to use the procedure of this report to treat this case, but it will not be done here.

2. Earlier Treatments

Landau's note is concerned with the behavior of an electron in a potential U . If $mUa^2/\hbar^2 \geq 1$, where a is the approximate extent, there may be bound states. Landau conjectures that there are two possible types of states of the electron-lattice system. In one the electron moves in a relatively undisturbed lattice, in the second one has a localized electron surrounded by a strong lattice polarization. If the second is energetically preferred, the claim is that the electron must overcome an activation energy before it can be trapped into the localized state so that at very low temperatures excess electrons introduced in the crystal cannot be trapped. These considerations are not restricted to polar crystals but are subject to the criticism that the nature and functional form of the potential U is not discussed, the lattice polarization is not treated as a dynamical system, and the statement concerning the activation energy is not proved.

Von Hippel²⁾ focusses attention on polar crystals and discusses the dynamics of the capture process. With the Einstein assumption of a constant frequency for all the modes of the optical branch, one can treat the separate unit cells as independent and use the Bohr theory of stopping power,

22) E. Engelhard, Ann. Physik 17, 501 (1933).

23) H. Fröhlich and N.F. Mott, Proc. Roy. Soc. A171, 496 (1939).

as has been done by Seeger and Teller²⁴⁾ in their theory of dielectric breakdown. A slow electron of kinetic energy $1/10$ ev has a velocity 2×10^7 cm/sec. and a Debroglie wavelength $\lambda = h/mv = 4 \times 10^{-7}$ cm and produces a coulomb field outside this region. It is necessary to introduce the critical distance v/ω , which for the case in question is $2 \times 10^7 / 6 \times 10^{12} \simeq 1/3 \times 10^{-5}$ cm. Ions more distant than this respond adiabatically to the electron motion and form a potential well for it. Ions lying between h/mv and v/ω are shock excited and receive energy from the electron. Thus the particle will slow down, decreasing the distance v/ω and increasing h/mv . This deepens the potential well and results in an effective mass because of the changing polarization carried with the electron. However, according to von Hippel, the potential well causes the kinetic energy of the electron to increase, so that v^2 increases, shortening the wavelength and allowing a deeper well to form. The stationary state is pictured as a localized electron with a shrunken Debroglie length. This picture contains substantial elements of truth, but is not quantitative and neglects the zero point motions of the ions and the possibility of translational motion of the "shrunken" electron. F.P.Z., in their critique of the self-trapping concept, assume that the shrinking process ceases when $h/mv = v/v = \rho$. They then estimate the energy of interaction as $-1/2 (1/n^2 - 1/\epsilon) e^2 \omega/v \simeq -1/2 (1/n^2 - 1/\epsilon) e^2 (2m\omega/h)^{1/2} \simeq -\alpha \hbar \omega$. In addition, the energy of interaction, according to this argument decreases only slowly with velocity, so that the effective mass is small. F.P.Z.'s argument can be criticized as being independent of the strength of interaction and in fact ceases to be valid for very strong interactions, i.e., the "shrinking" effect must be taken into account. The limitations of this argument have their counterpart in the mathematical technique used to treat the Hamiltonian for the system, i.e., F.P.Z. restrict themselves to a wave function which con-

24) R. J. Seeger and E. Teller, Phys. Rev. 54, 515 (1938); 56, 352 (1939).

tains only zero or one quantum terms.

Mott and Gurney³⁾ assert that self trapping is possible in all polar crystals and that a series of discrete levels exist because the potential falls off as $1/r$. This again neglects the zero point motions and quantum fluctuations of the lattice vibrations.

The preceding discussions are only qualitative. To give an adequate discussion of the problem one must treat the electron and the lattice particles as dynamical systems and write a Hamiltonian describing the particle and lattice motions and their interactions. This has been done for polar crystals by Fröhlich^{5, 25)} in connection with the theory of dielectric breakdown and discussed and improved by Fröhlich and Seitz²⁶⁾ and Callen²⁷⁾. The total Hamiltonian may be written as

$$\mathcal{H} = \mathcal{H}_{\text{particle}} + \mathcal{H}_{\text{interaction}} + \mathcal{H}_{\text{field}}. \quad (1)$$

The particle portion is taken as $p^2/2m_c$ corresponding to a particle of effective mass m_c . The field portion is a sum over the kinetic energies of the ions and the mutual potential energies corresponding to a given set of displacements, the force constants depending on the details of the interactions. For small vibrations the system is redescribed in terms of normal modes in which the frequencies and relative amplitudes of the ions depend in a complicated way on the interactions. The interaction energy of electron and lattice oscillations also depends in general on the detailed distortions occurring during the ionic motions. It is possible, however, to present explicit expressions if one restricts oneself to the modes with wavelength large compared to the lat-

25) H. Fröhlich, Proc. Roy. Soc. A160, 230 (1937).

26) H. Fröhlich and F. Seitz, Phys. Rev. 79, 526 (1950).

27) H. Callen, Phys. Rev. 76, 1394 (1949).

tice period. This will be a fair approximation for the case of slow electrons in a polar crystal.

For a diatomic crystal there are three optical branches and three acoustical branches. If we let $b_{\underline{k}, j}$ be the normal co-ordinate of the j 'th branch and \underline{k} the wavevector, we have for the energy connected with the lattice vibrations

$$\mathcal{H}_{\text{field}} = \frac{1}{2} \sum_{j=1}^6 \sum_{\underline{k}} (b_{\underline{k}j}^2 + \omega_{\underline{k}j}^2 b_{\underline{k}j}^2) \quad (2)$$

For long wavelengths two of the three optical or acoustical branches represent transverse modes and one a longitudinal mode. The $b_{\underline{k}j}$ are connected with the displacements of the ions by the equations

$$\begin{aligned} \hat{U}_+(\underline{r}) &= \sum_{j=1}^6 \sum_{\underline{k}} U_{+\underline{k}j}(\underline{r}) \\ \hat{U}_-(\underline{r}) &= \sum_{j=1}^6 \sum_{\underline{k}} U_{-\underline{k}j}(\underline{r}) \end{aligned} \quad (3)$$

where

$$\begin{aligned} \hat{U}_{+\underline{k}j}(\underline{r}) &= \left(\frac{2}{M_+ N} \right)^{1/2} b_{\underline{k}j} \xi_{+\underline{k}j} \begin{Bmatrix} \sin \\ \cos \end{Bmatrix} (\underline{k} \cdot \underline{r}) \\ \hat{U}_{-\underline{k}j}(\underline{r}) &= \left(\frac{2}{M_- N} \right)^{1/2} b_{\underline{k}j} \xi_{-\underline{k}j} \begin{Bmatrix} \sin \\ \cos \end{Bmatrix} (\underline{k} \cdot \underline{r}) \end{aligned} \quad (4)$$

$\xi_{+\underline{k}j}$ and $\xi_{-\underline{k}j}$ are vectors pointing in the direction of polarization. They determine the relative amplitudes of the ions and satisfy $\xi_{+\underline{k}j}^2 + \xi_{-\underline{k}j}^2 = 1$. M_+ and M_- are the masses of the positive and negative ions and N is the number of unit cells in the quantization box. The above decomposition is into standing waves and the notation $\begin{Bmatrix} \sin \\ \cos \end{Bmatrix} (\underline{k} \cdot \underline{r})$ means that the sin goes with $-\underline{k}$ when the cos goes with \underline{k} .

In a polar crystal the perturbing forces acting on an electron are of two types. There is first the distortion of the electron clouds of the nearby ions.

This interaction is not important for estimating the effective mass of slow electrons since the response of the electron cloud is rapid and does not depend appreciably on the electron speed. Second, the moving ions, together with the electron-cloud distortion, produce a long range dipole component. This has been estimated^{25, 27)} for long wavelength as follows: The polarization produced by a normal mode \vec{k} is the dipole moment per unit volume

$$\vec{P}_{\vec{k}j}(\vec{r}) = \frac{e^*}{2a^3} (\vec{U}_{+\vec{k}j}(\vec{r}) - \vec{U}_{-\vec{k}j}(\vec{r})) \quad , \quad (5)$$

where e^* differs from the electronic charge because of the dipole contributions of the electronic clouds. For long wavelengths the polarization varies slowly from one unit cell to the next. The potential produced is determined from Poisson's equation

$$\nabla^2 \phi_{\vec{k}j} = 4\pi \vec{\nabla} \cdot \vec{P}_{\vec{k}j} \quad . \quad (6)$$

From this equation one concludes that the transverse modes produce no perturbing potential. In addition, one can show that the amplitudes $\xi_{+\vec{k}}$ and $\xi_{-\vec{k}}$ for acoustic waves of long length are such that $P_{\vec{k}}$ is very small. For short acoustic waves the dipole component is appreciable. One is thus left with the longitudinal optical modes of long wavelength as the principal source of the perturbing potential for slow electrons. For longitudinal waves of infinite length we have

$$\frac{\xi_{+\vec{k}}}{M_+^{1/2}} - \frac{\xi_{-\vec{k}}}{M_-^{1/2}} = \left(\frac{1}{M_+} + \frac{1}{M_-} \right)^{1/2} = \frac{1}{\mu^{1/2}} \quad ,$$

where μ is the reduced mass of the ions. The total perturbing potential is then taken to be

$$\phi = \sum_{\vec{k}} \phi_{\vec{k}} = \sum_{\vec{k}} \frac{2\pi e^*}{a^3 k} \left(\frac{2}{\mu N} \right)^{1/2} b_{\vec{k}} \begin{Bmatrix} -\cos \\ \sin \end{Bmatrix} (\vec{k} \cdot \vec{r}) \quad , \quad (7)$$

and the total Hamiltonian for the particle and lattice vibrations is

$$\mathcal{H} = \frac{p^2}{2m_c} + e\phi(\vec{r}_e) + \frac{1}{2} \sum \left\{ \dot{b}_{\underline{k}}^2 + \omega_{\underline{k}}^2 b_{\underline{k}}^2 \right\} \quad (8)$$

The preceding derivation depends very essentially on the assumption that the wavelengths of importance in the problem are of long wavelength so that sums over the shortwave portions give small contributions. Additional assumptions are made in connecting the constants e^* and $\omega_{\underline{k}} = \omega$ with experiment. It has been pointed out by Fröhlich and Mott²³⁾ and Lyddane, Sachs and Teller²⁸⁾ that ω for the longitudinal optical modes of infinite wavelength is higher than that for the corresponding transverse modes (reststrahlen) because of the additional restoring force due to the macroscopic field created by the motion of the ions in a longitudinal mode. Under the assumption that the field acting on the ions is \vec{E} , rather than an internal field more appropriate to the face-centered cubic lattice, it is possible to derive the equation $\omega^2 = \omega_t^2 \frac{\epsilon}{n^2}$, where ω_t is the reststrahl frequency. The effective charge e^* can also be connected²⁷⁾ with experimentally observable constants by

$$\omega_t^2 = \left(\frac{2\pi e^{*2}}{\mu a^3} \right) \left(\frac{n^4}{\epsilon - n^2} \right)$$

The above Hamiltonian is written in terms of standing wave co-ordinates. The $b_{\underline{k}}$ and $\dot{b}_{\underline{k}}$ can be shown to be canonical co-ordinates and momenta and it is possible to perform a canonical transformation from these to a set of running wave co-ordinates. With

$$\left. \begin{aligned} X_{\underline{k}} &= \left(\frac{b_{\underline{k}}}{\sqrt{2M}} + \frac{\dot{b}_{-\underline{k}}}{\sqrt{2M\omega^2}} \right) \\ X_{-\underline{k}} &= \left(\frac{\dot{b}_{-\underline{k}}}{\sqrt{2M\omega^2}} - \frac{b_{\underline{k}}}{\sqrt{2M}} \right) \end{aligned} \right\} \left. \begin{aligned} Y_{\underline{k}} &= \left(\sqrt{\frac{M}{2}} \dot{b}_{\underline{k}} - \sqrt{\frac{M\omega^2}{2}} b_{-\underline{k}} \right) \\ Y_{-\underline{k}} &= - \left(\sqrt{\frac{M}{2}} \dot{b}_{\underline{k}} + \sqrt{\frac{M\omega^2}{2}} b_{-\underline{k}} \right) \end{aligned} \right\} \quad (9)$$

28) R.H. Lyddane, R.G. Sachs and E. Teller, Phys. Rev. 59, 673 (1941).

where

$$\frac{1}{M\omega^2} = \frac{1}{4\pi} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \quad (10)$$

The Hamiltonian becomes

$$\begin{aligned} \mathcal{H} = & \frac{p^2}{2m_c} + \frac{4\pi e}{\sqrt{V}} \sum_{\underline{k}} \frac{1}{k} (X_{\underline{k}} \sin \hat{\underline{k}} \cdot \hat{\underline{q}} + \frac{Y_{\underline{k}}}{M\omega} \cos \hat{\underline{k}} \cdot \hat{\underline{q}}) \\ & + \frac{1}{2} \sum_{\underline{k}} \left(M\omega^2 X_{\underline{k}}^2 + \frac{Y_{\underline{k}}^2}{M} \right) \quad (11) \end{aligned}$$

This is the starting point of most discussions of slow electron behavior in polar crystals. The basic restriction to long wavelengths becomes increasingly poor for increasing interaction strength as the polarization surrounding the electron shrinks to atomic dimensions. However, the Hamiltonian appears adequate to settle some of the basic conceptual conflicts in the self-trapping problem.

The expression Eq.(11) can be treated by classical mechanics. One writes Hamilton's equations of motion

$$\left. \begin{aligned} \frac{d\hat{\underline{p}}}{dt} &= -\frac{\partial \mathcal{H}}{\partial \hat{\underline{q}}} = -\frac{4\pi e}{\sqrt{V}} \sum_{\underline{k}} \frac{\hat{\underline{k}}}{k} \left(X_{\underline{k}} \cos \hat{\underline{k}} \cdot \hat{\underline{q}} - \frac{Y_{\underline{k}}}{M\omega} \sin \hat{\underline{k}} \cdot \hat{\underline{q}} \right) \\ \frac{d\hat{\underline{q}}}{dt} &= \frac{\partial \mathcal{H}}{\partial \hat{\underline{p}}} = \frac{\hat{\underline{p}}}{m_c} \\ \frac{dY_{\underline{k}}}{dt} &= -\frac{\partial \mathcal{H}}{\partial X_{\underline{k}}} = -\frac{4\pi e}{\sqrt{V}} \frac{1}{k} \sin \hat{\underline{k}} \cdot \hat{\underline{q}} + M\omega^2 X_{\underline{k}} \\ \frac{dX_{\underline{k}}}{dt} &= \frac{\partial \mathcal{H}}{\partial Y_{\underline{k}}} = \frac{4\pi e}{\sqrt{V}} \frac{1}{k} \frac{\cos \hat{\underline{k}} \cdot \hat{\underline{q}}}{M\omega} + \frac{Y_{\underline{k}}}{M} \end{aligned} \right\} \quad (12)$$

It is difficult to solve these nonlinear equations for a general set of initial

conditions. The equations have $2(2N + 3)$ independent integrals of motion and a particular solution is identified by specifying the values of the integrals. It is possible, however, to discuss a particular type of solution in which there is a definite relation between the energy integral and the momentum integrals. This solution represents an electron moving with constant velocity and the oscillators undergoing purely forced motion. By studying the relation between the energy and total momentum, one can assign an "effective mass" to the electron arising from its interaction with the vibrations. This type of solution should be the classical analogue of the quantum solution for the lowest states where no free quanta are present. We take

$$\left. \begin{aligned} \vec{p} &= \vec{p}_0 = \text{constant} \\ \vec{q} &= \frac{\vec{p}_0}{m_c} t + \vec{q}_0 \\ X_{\underline{k}} &= m_c \frac{4\pi e}{\sqrt{V} k} \frac{1}{M\omega} \frac{1}{\frac{\vec{k} \cdot \vec{p}_0}{m_c} - \omega} \sin \vec{k} \cdot \left(\frac{\vec{p}_0}{m} t + \vec{q}_0 \right) \\ \frac{Y_{\underline{k}}}{M\omega} &= \frac{4\pi e}{\sqrt{V} k} \frac{1}{\frac{\vec{k} \cdot \vec{p}_0}{m_c} - \omega} \cos \vec{k} \cdot \left(\frac{\vec{p}_0}{m} t + \vec{q}_0 \right) \end{aligned} \right\} \quad (13)$$

The expression for $X_{\underline{k}}$ indicates that the field amplitudes must be assigned large values for those waves for which the particle speed is close to the wave speed. If we restrict ourselves to very slow particle speeds, $\vec{k} \cdot \vec{p}_0 / m_c < \omega$ even for the shortest waves (k_{max}) corresponding to lattice dimensions, i.e., there are no trapped electrons. For these very slow particles we should expect the effective mass to be unity since all of the ions are excited adiabatically and there is no change in polarization with particle speed. This may be verified by writing the momentum

$$\vec{\lambda} = \vec{p} + \sum_{\underline{k}} \frac{\vec{k}}{\omega} \left\{ \frac{M\omega^2 X_{\underline{k}}^2}{2} + \frac{Y_{\underline{k}}^2}{2M} \right\} = \vec{p}_0 + \sum_{\underline{k}} \frac{\vec{k}}{\omega} \frac{M\omega^2}{2} \left(\frac{\frac{4\pi e}{\sqrt{V}kM\omega}}{\left(\frac{\vec{k} \cdot \vec{p}_0}{m} - \omega \right)} \right)^2 \quad (14)$$

and the energy

$$E = \frac{p_0^2}{2m} + \sum_{\underline{k}} \left(\frac{\frac{4\pi e}{\sqrt{V}k}}{\frac{\vec{k} \cdot \vec{p}_0}{m} - \omega} \right)^2 \frac{1}{M\omega} + \frac{1}{2} \sum_{\underline{k}} M\omega^2 \left(\frac{\frac{4\pi e}{\sqrt{V}k}}{\frac{\vec{k} \cdot \vec{p}_0}{m} - \omega} \right)^2 \frac{1}{M\omega} \quad (15)$$

By eliminating \vec{p}_0 we can find a relation between E and λ^2 which for slow particles is characteristic of a free electron.

Let us consider the case of particles at rest. Then $\vec{p}_0 = \vec{\lambda} = 0$ and $E = -\frac{1}{2} \sum_{\underline{k}} \left(\frac{4\pi e}{\sqrt{V}k} \right)^2 \frac{1}{M\omega^2}$. The energy thus depends on the details of the short-wave cutoff. Following F.P.Z. we can compute the potential produced at a point \vec{r} by an electron at \vec{q}_0 . Inserting the values for $X_{\underline{k}}$ and $Y_{\underline{k}}$ from Eqs. (13) we find

$$\begin{aligned} \phi(\vec{r}) &= \frac{4\pi}{V^{1/2}} \sum_{\underline{k}} \frac{1}{k} (X_{\underline{k}} \sin \vec{k} \cdot \vec{r} + \frac{Y_{\underline{k}}}{M\omega} \cos \vec{k} \cdot \vec{r}) \\ &= \frac{-16\pi^2 e}{VM\omega^2} \sum_{\underline{k}} \frac{\cos(\vec{k} \cdot \vec{r} - \vec{q}_0)}{k^2} \\ &= -\frac{e}{|\vec{r} - \vec{q}_0|} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \end{aligned} \quad (16)$$

This is the potential of a point charge in a dielectric and verifies the choice

$$\frac{1}{M\omega^2} = \frac{1}{4\pi} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right).$$

Fröhlich and Pelzer²⁸⁾ have presented another treatment of the behavior of a classical point charge interacting with the polar modes. The electron is

assumed to move with uniform velocity and the response of the oscillators is calculated. The electron velocity is high so that energy loss associated with trapping must occur. Fröhlich and Pelzer²⁹⁾ treat this phenomenon schematically, neglecting electron recoil. In addition, they compute the energy carried along with the electron and find an effective mass increasing rapidly with decreasing electron speed.

Deviations from classical behavior are expected in two different ways. First, one must consider the wave character of the electron. This leads one to expect that at least for weak interactions the cutoff will be given by the Debroglie wavelength of the electron rather than the lattice spacing. Second, there are quantum and zero point fluctuations in the field of the polarization quanta. Classical mechanics is expected to become valid in the limit of infinitely great interactions, but it is possible that the two types of quantum effects become unimportant at different values of the coupling constant. Thus, one can imagine a semiclassical treatment in which one system is treated classically, the other quantummechanically. The treatments of Pekar³⁰⁾ and of Landau and Pekar⁶⁾ are of this type.

Pekar describes the electron by a wave function $\psi(\vec{r})$ which produces a dielectric displacement

$$\vec{D}(\vec{r}) = \int |\psi(\vec{r}')|^2 \frac{(\vec{r} - \vec{r}')}{|\vec{r} - \vec{r}'|^3} d\tau' \quad (17)$$

The displacement polarizes the lattice, and, in a continuum theory,

$$\vec{P}(\vec{r}) = \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \frac{\vec{D}(\vec{r})}{4\pi} \quad (18)$$

29) H. Fröhlich and H. Pelzer, British Elect. and Allied Ind. Res. Assoc., Tech. Rep. LIT, 184 (1948).

30) S. Pekar, J. Physics USSR 10, 341 (1946).

The interaction energy of electron and polarization is

$$V = - \int \vec{P} \cdot \vec{D} d\tau \quad , \quad (19)$$

and the electron wave function satisfies the self-consistent Schrödinger equation

$$\frac{-\hbar^2}{2m_c} \nabla^2 \psi + V \psi = E \psi \quad . \quad (20)$$

Pekar finds

$$\left. \begin{aligned} \psi(\vec{r}) &\approx 0.123 a^{3/2} (1 + ar + 0.45 a^2 r^2) e^{-ar} \\ a &= 0.66 \frac{m_e e^2}{\hbar^2} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \\ E &\approx -0.164 \frac{m_c e^4}{\hbar^2} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right)^2 = -0.33 a^2 \hbar \omega \end{aligned} \right\} \quad , \quad (21)$$

and shows that this represents the optical activation energy. The thermal "dissociation energy" is equal to the total energy depression and is shown to be

$$E_{th} \approx -0.11 a^2 \hbar \omega \quad . \quad (22)$$

Actually, there are two corrections which should be made. First the continuum states are also depressed. Second, even in absence of interaction, the continuum lies $\hbar\omega$ above the ground level so that one should add $\hbar\omega$ to the energy depression to obtain E_{th} . Pekar's expression becomes valid when the energy depression is large compared to a quantum, i.e., when $0.1 a^2 \gg 1$ or $a \gg 3$. For weaker coupling, zero point motions and quantum fluctuations are important.

In a later paper⁷⁾ Pekar derived this expression on the basis of a completely quantummechanical argument. Starting from the Hamiltonian

Eq.(8) in the standing wave representation, he assumed a trial function of the product form

$$\Phi(\vec{r}, \dots q_{\underline{k}}) = \psi(\vec{r}) \prod_{\underline{k}} \Phi_{\underline{k}}(q_{\underline{k}}) \quad , \quad (23)$$

where

$$q_{\underline{k}} = P_{\underline{k}} \sqrt{\frac{M\omega}{\hbar}}$$

The forms of the functions $\psi(\vec{r})$ and $\Phi_{\underline{k}}(q_{\underline{k}})$ are chosen so as to minimize the energy. $\Phi_{\underline{k}}$ satisfies a Euler-Lagrange equation and is found to be

$$\phi_{\underline{k}} = A_{\underline{k}} \exp \left[-\frac{1}{2} (q_{\underline{k}} - q_{\underline{k}0})^2 \right] \quad . \quad (24)$$

where $A_{\underline{k}}$ is a normalization constant and $q_{\underline{k}0} = D_{\underline{k}} \sqrt{\frac{M\omega}{\hbar}}$ with $D_{\underline{k}} =$

$$\sqrt{\frac{2}{V}} \int D(\vec{r}) \left\{ \frac{\cos(\vec{k} \cdot \vec{r})}{\sin(\vec{k} \cdot \vec{r})} \right\} d\vec{r} \quad . \quad \text{This is the equation of a harmonic oscillator}$$

with its equilibrium position displaced by an amount depending on the electronic wave function $\psi(\vec{r})$. Pekar showed that $\psi(\vec{r})$ is the same function used in the semiclassical treatment and that the total energy (neglecting zero point energy) is again $-0.11 \alpha^2 \hbar \omega$. The importance of this calculation lies in the demonstration that for large α the energy depression varies much more rapidly than linearly with α . The treatment is based on the variational method so that the true energy must be even lower.

To find the effective mass of a moving polaron in a semiclassical approximation, Landau and Pekar⁶⁾ studied a special, purely 'forced' motion. They assumed $\psi = \psi(\vec{r} - \vec{V}t)$, $\hat{D} = \hat{D}(\vec{r} - \vec{V}t)$, $\hat{p} = \hat{p}(\vec{r} - \vec{V}t)$, and developed the expectation value of the energy in powers of the velocity. One obtains $m^* = 27(\alpha/b)^4 m_c$. An attempt by Pekar⁷⁾ to put this treatment on a quantum-mechanical footing is not convincing but the more recent work of Bogoliubov¹⁷⁾

and Tyablikov¹⁸⁾ gives the same value as the first step in a systematic adiabatic approximation procedure. The validity of the semiclassical procedure might be checked by examining the higher terms in the adiabatic procedure, but this has not been done. However, there does not appear to be reason for doubting the validity at very large α where quantum fluctuations are unimportant.

Let us now briefly look at the problem from the purely quantum-mechanical point of view and in the approximation of weak interaction. The energy levels in absence of interaction are given by

$$E(\alpha = 0) = \frac{(\hat{\lambda} - \sum_{\mathbf{k}} n_{\mathbf{k}} \hbar \mathbf{k})^2}{2m} + \sum_{\mathbf{k}} (n_{\mathbf{k}} + 1/2) \hbar \omega_{\mathbf{k}} \quad , \quad (25)$$

and is a function of the quantum numbers $\hat{\lambda}$ and $N_{\mathbf{k}}$. For a one-dimensional case we may plot E vs. λ ³¹⁾ and find schematically Fig. 1. The point of intersection of the discrete state with the continuum is

$$\lambda = \sqrt{\frac{2m_c \omega}{\hbar}}$$

or the critical distance of F.P.Z.

Upon introducing the interaction the ground curve is depressed. The portion of the curve belonging to larger values of λ is closer to the higher state curves and is therefore depressed more than the portion near $\lambda = 0$. One thus obtains a changed curvature and effective mass. For very weak interactions it is possible to apply second order perturbation theory and one obtains for the energy levels (dropping the zero-point oscillator energies)

$$E = -\frac{\lambda^2}{2m_c} - (\alpha \hbar \omega) \frac{(2m_c \hbar \omega)^{1/2}}{\lambda} \sin^{-1} \frac{\lambda}{(2m_c \hbar \omega)^{1/2}} \quad .$$

31) Cf. E.P. Gross, Phys. Rev. 84, 818 (1951).

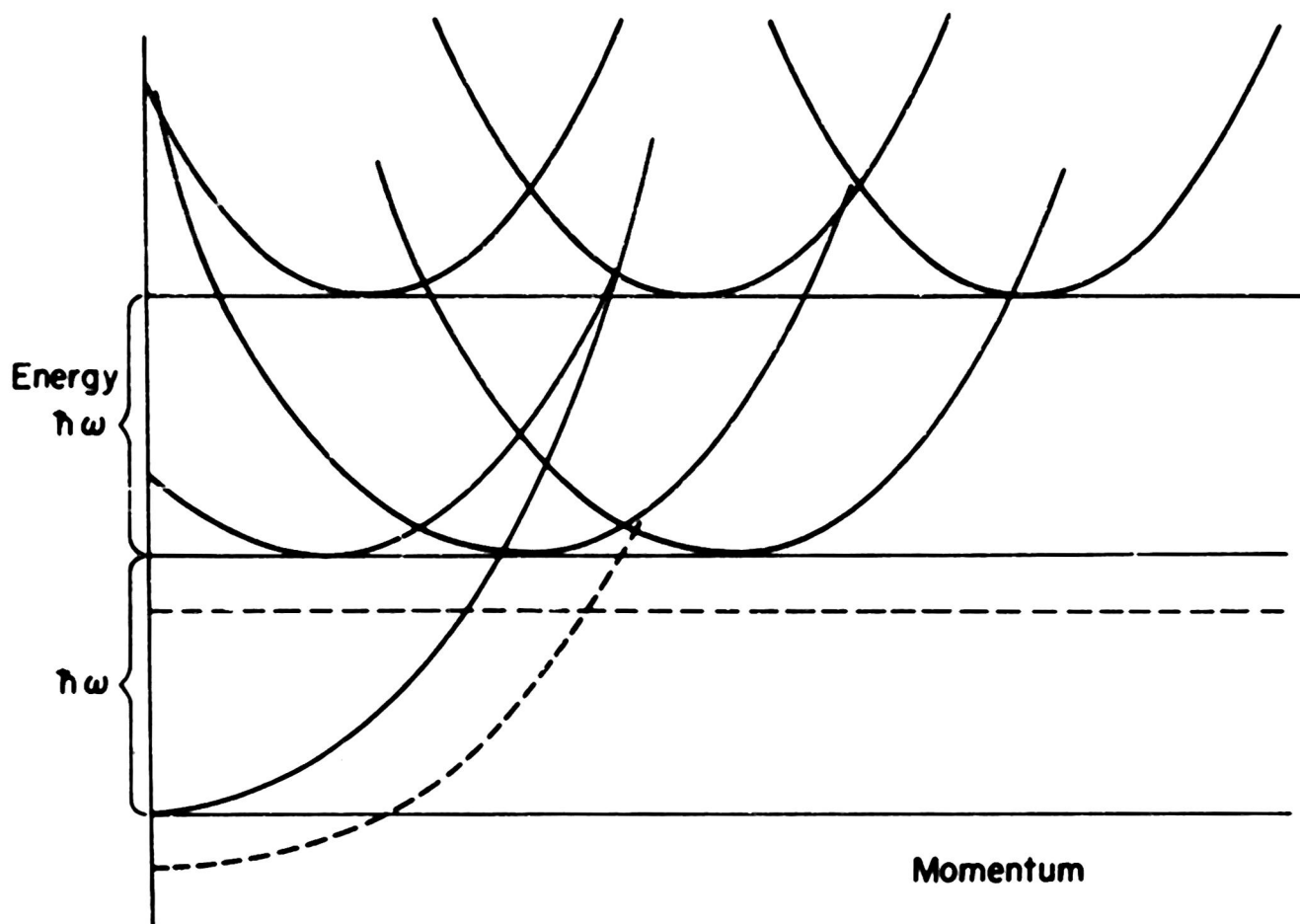


Fig. 1. Energy vs. momentum (schematic).

For small λ

$$E \simeq \frac{\lambda^2}{2m_c} - (a\hbar\omega) \left\{ 1 + \frac{1}{6} \frac{\lambda^2}{2m_c \hbar\omega} \right\} . \quad (26)$$

so that the effective mass is $m^* = m_c / (1 - a/6)$.

For a one-dimensional model to be studied in detail later, second order perturbation theory gives

$$\left. \begin{aligned} E &= \frac{\lambda^2}{2m_c} - (\beta^2 \pi) \hbar\omega \frac{1}{(1 - \lambda^2/2m_c)^{1/2}} \\ m^* &= m_c / (1 - \beta^2 \pi/2) \end{aligned} \right\} . \quad (27)$$

These formulas break down for strong interactions and it is necessary to include the effects of higher quanta. This is done in the next section.

3. Schrödinger Equation in Fock Representation

In accordance with the discussion of Section 2 we shall take as the Hamiltonian for an electron interacting with the polar optical modes

$$\mathcal{H} = \frac{p^2}{2m} + \sum_{\underline{k}} g_{\underline{k}} (X_{\underline{k}} \sin \hat{\underline{k}} \cdot \hat{\underline{q}} + \frac{Y_{\underline{k}}}{M\omega} \cos \hat{\underline{k}} \cdot \hat{\underline{q}}) + \frac{1}{2} \sum_{\underline{k}} (M\omega^2 X_{\underline{k}}^2 + \frac{Y_{\underline{k}}^2}{M}). \quad (11)$$

In the quantum theory it is possible to use the approach of F.P.Z. which regards \mathcal{H} as operating on a wave function of the form $\Psi(q, X_{\underline{k}})$ and to replace p and $1/\underline{k}$ by the operators $-i\hbar \partial/\partial q$ and $-i\hbar \partial/\partial X_{\underline{k}}$. In this report we shall adopt an alternative approach due to Fock¹⁰⁾ which takes advantage of the fact that the polarization quanta form a Bose-Einstein system with symmetric wave functions. Fock has shown that a Hamiltonian of the above type can be regarded as operating on a wave functional which has as components functions giving probabilities of various states in which a given number of quanta are present. Thus the wave functional

$$\Phi = (X_0(\hat{\underline{q}}), X_1(\hat{\underline{k}}, \hat{\underline{q}}), X_2(\hat{\underline{k}}_1, \hat{\underline{k}}_2, \hat{\underline{q}}), \dots) \quad (28)$$

has the following interpretation: $|X_0(\hat{\underline{q}})|^2 d\hat{\underline{q}}$ is the probability that an electron is found at $\hat{\underline{q}}$ in a region $d\hat{\underline{q}}$ and no quanta are present; $|X_1(\hat{\underline{k}}_1, \hat{\underline{q}})|^2 d\hat{\underline{k}}_1 d\hat{\underline{q}}$ is the probability that there is one quantum of wave vector $\hat{\underline{k}}_1$ in a range $d\hat{\underline{k}}_1$ and an electron at $\hat{\underline{q}}$ in a range $d\hat{\underline{q}}$, etc. The sum of the absolute squares of the components when integrated over the configuration ranges is normalized to unity.

With this representation one writes the Schrödinger equation $(\mathcal{H} - E) \Phi = 0$ as an infinite chain of integral equations. It is first conveni-

ent to introduce the co-ordinates C_k , C_k^* defined by

$$\left. \begin{aligned} C_k &= \sqrt{\frac{M\omega}{2\hbar}} \left(X_k + i \frac{Y_k}{M\omega} \right) \frac{1}{i} \\ C_k^* &= \sqrt{\frac{M\omega}{2\hbar}} \left(X_k - i \frac{Y_k}{M\omega} \right) i \end{aligned} \right\} \quad \left. \begin{aligned} X_k &= (C_k - C_k^*) i \sqrt{\frac{\hbar}{2M\omega}} \\ Y_k &= (C_k + C_k^*) \sqrt{\frac{\hbar}{2M\omega}} \end{aligned} \right\} \quad (29)$$

We note that C_k and C_k^* are not canonical conjugates but, instead, satisfy the commutation rules $[C_k, C_k^*] = \delta_{kk}$. In addition, C_k^* is the complex conjugate of C_k since X_k and $1/k$ are real. In terms of these co-ordinates we may rewrite the Hamiltonian as

$$\begin{aligned} \mathcal{H} &= \frac{p^2}{2m} + \sum_k \frac{\hbar}{2M\omega}^{1/2} g_k \left(C_k e^{i\vec{k} \cdot \vec{q}} + C_k^* e^{-i\vec{k} \cdot \vec{q}} \right) + \sum_k \hbar\omega_k C_k^* C_k \\ &\quad - \sum_k \frac{\hbar\omega_k}{2} \end{aligned} \quad (30)$$

The zero of energy may be chosen so that the contribution of the zero point oscillations drops out and one obtains, following Fock and Tomonaga,

$$\begin{aligned} \left\{ E - \frac{p^2}{2m} \right\} \chi_0(\vec{q}) &= \sum_{\vec{k}_1} g(\vec{k}_1) \left(\frac{\hbar}{2M\omega} \right)^{1/2} e^{-i\vec{k}_1 \cdot \vec{q}} \chi_1(\vec{k}_1, \vec{q}) \\ \left\{ E - \frac{p^2}{2m} - \hbar\omega \right\} \chi_1(\vec{k}_1, \vec{q}) &= g(\vec{k}_1) \left(\frac{\hbar}{2M\omega} \right)^{1/2} e^{i\vec{k}_1 \cdot \vec{q}} \chi_0(\vec{q}) \\ &\quad + 2^{1/2} \left(\frac{\hbar}{2M\omega} \right)^{1/2} \sum_{\vec{k}_2} \chi_2(\vec{k}_1, \vec{k}_2, \vec{q}) g(\vec{k}_2) e^{-i\vec{k}_2 \cdot \vec{q}} \\ \left\{ E - \frac{p^2}{2m} - 2\hbar\omega \right\} \chi_2(\vec{k}_1, \vec{k}_2, \vec{q}) &= \frac{1}{2^{1/2}} \left(\frac{\hbar}{2M\omega} \right)^{1/2} \left\{ g(\vec{k}_2) e^{i\vec{k}_2 \cdot \vec{q}} \chi_1(\vec{k}_1, \vec{q}) \right. \\ &\quad \left. + g(\vec{k}_1) e^{i\vec{k}_1 \cdot \vec{q}} \chi_1(\vec{k}_2, \vec{q}) \right\} \end{aligned} \quad (31)$$

This is the coupled set of equations cut off so as to include terms with two quanta or less. In this set p is understood to be the differential operator $-i\hbar \frac{\partial}{\partial q}$. Let us introduce

$$\begin{aligned}\zeta_1(\hat{k}_1 \hat{q}) &= e^{-i\hat{k}_1 \cdot \hat{q}} \chi_1(\hat{k}_1 \hat{q}) \\ \zeta_2(\hat{k}_1 \hat{k}_2 \hat{q}) &= e^{-i(\hat{k}_1 + \hat{k}_2) \cdot \hat{q}} \chi_2(\hat{k}_1 \hat{k}_2 \hat{q})\end{aligned}\quad (32)$$

If one then assumes

$$\begin{aligned}\chi_0(\hat{q}) &= \chi_0 e^{i\hat{\lambda} \cdot \hat{q}} \\ \zeta_1(\hat{k}_1 \hat{q}) &= \zeta_1(\hat{k}_1) e^{i\hat{\lambda} \cdot \hat{q}}\end{aligned}\quad (33)$$

$$\zeta_2(\hat{k}_1 \hat{k}_2 \hat{q}) = \zeta_2(\hat{k}_1 \hat{k}_2) e^{i\hat{\lambda} \cdot \hat{q}}$$

Eq.(31) becomes

$$\begin{aligned}\left(E - \frac{\hbar^2 \lambda^2}{2m}\right) \chi_0 &= \sum_{\hat{k}_1} g(\hat{k}_1) \left(\frac{\hbar}{2M\omega}\right)^{1/2} \zeta_1(\hat{k}_1) \\ \left\{E - \hbar\omega - \frac{\hbar^2}{2m} (\hat{\lambda} + \hat{k}_1)^2\right\} \zeta_1(\hat{k}_1) &= g(\hat{k}_1) \left(\frac{\hbar}{2M\omega}\right)^{1/2} \chi_0 + 2^{1/2} \left(\frac{\hbar}{2M\omega}\right)^{1/2} \\ &\quad \sum_{\hat{k}_2} g(\hat{k}_2) \zeta_2(\hat{k}_1 \hat{k}_2)\end{aligned}\quad (34)$$

$$\begin{aligned}\left\{E - 2\hbar\omega - \frac{\hbar^2}{2m} (\hat{\lambda} + \hat{k}_1 + \hat{k}_2)^2\right\} \zeta_2(\hat{k}_1 \hat{k}_2) &= \frac{1}{2^{1/2}} \left(\frac{\hbar}{2M\omega}\right)^{1/2} \left\{g(\hat{k}_2) \zeta_1(\hat{k}_1) \right. \\ &\quad \left. + g(\hat{k}_1) \zeta_1(\hat{k}_2)\right\}.\end{aligned}$$

Let us first examine these equations when the amplitudes of the two quantum terms are set equal to zero. One obtains from Eq.(34b)

$$\zeta_1(\vec{k}_1) = \frac{g(\vec{k}_1) \left(\frac{\hbar}{2M\omega} \right)^{1/2} \chi_0}{E - \hbar\omega - \frac{\hbar^2}{2m} (\vec{\lambda} + \vec{k})^2} \quad (35)$$

Inserting this into Eq.(34a) we find the expression for the determination of the energy of the lowest states

$$E - \frac{\hbar^2 \lambda^2}{2m} = \sum_{\vec{k}} \frac{g^2(\vec{k}_1) \left(\frac{\hbar}{2M\omega} \right)}{E - \hbar\omega - \frac{\hbar^2}{2m} (\vec{\lambda} + \vec{k})^2} \quad (36)$$

This is exactly the expression obtained by F. P. Z.

To find the wave functions and energy levels in the two quantum approximation, one inserts $\zeta_2(\vec{k}_1, \vec{k}_2)$ from Eq.(34c) into Eq.(34b). We thus find the pair of integral equations

$$\begin{aligned} \left(E - \frac{\hbar^2 \lambda^2}{2m} \right) \chi_0 &= \sum_{\vec{k}} g(\vec{k}) \left(\frac{\hbar}{2M\omega} \right)^{1/2} \zeta_1(\vec{k}_1) \\ \left\{ E - \hbar\omega - \frac{\hbar^2}{2m} (\vec{\lambda} + \vec{k})^2 - \frac{\hbar}{2M\omega} \sum_{\vec{x}} \frac{g^2(\vec{x})}{E - 2\hbar\omega - \frac{\hbar^2}{2m} (\vec{\lambda} + \vec{k} + \vec{x})^2} \right\} \zeta_1(\vec{k}) & \quad (37) \\ &= g(\vec{k}) \left(\frac{\hbar}{2M\omega} \right)^{1/2} \chi_0 + g(\vec{k}) \left(\frac{\hbar}{2M\omega} \right) \sum_{\vec{x}} \frac{g(\vec{x}) \zeta_1(\vec{x})}{E - 2\hbar\omega - \frac{\hbar^2}{2m} (\vec{\lambda} + \vec{k} + \vec{x})^2} \end{aligned}$$

The method which has been adopted to solve Eqs.(37) is to treat Eq.(37b) as an inhomogeneous integral equation and to solve for $\zeta_1(\vec{k})$ by iteration, i.e., by finding the Liouville-Neumann series. The expression for $\zeta_1(\vec{k})$ is then inserted in the right-hand side of Eq.(37a) giving an implicit expression for $E(\lambda)$. For an integral equation of type

$$\phi(\hat{\mathbf{x}}) = h(\hat{\mathbf{x}}) + \int K(\hat{\mathbf{x}}, \hat{\mathbf{y}}) \phi(\hat{\mathbf{y}}) d\hat{\mathbf{y}} \quad (38)$$

with sufficiently regular kernel $K(\hat{\mathbf{x}}, \hat{\mathbf{y}})$, the condition³²⁾ for convergence of the Liouville-Neumann series is

$$\iint |K(\hat{\mathbf{x}}, \hat{\mathbf{y}})|^2 d\hat{\mathbf{x}} d\hat{\mathbf{y}} \leq 1 \quad (39)$$

For Eq.(37b) we may find the condition of convergence by introducing

$$\pi(\hat{\mathbf{k}}) = \left\{ E - \hbar\omega - \frac{\hbar^2}{2m} (\hat{\lambda} + \hat{\mathbf{k}})^2 - \frac{\hbar}{2M\omega} \sum_{\hat{\mathbf{x}}} \frac{g^2(\hat{\mathbf{x}})}{E - 2\hbar\omega - \frac{\hbar^2}{2m} (\hat{\lambda} + \hat{\mathbf{k}} + \hat{\mathbf{x}})^2} \right\} \zeta_1(\hat{\mathbf{k}}) \quad (40)$$

Then

$$K(\hat{\mathbf{k}}_1, \mathbf{x}) = \frac{g(\hat{\mathbf{k}}) g(\hat{\mathbf{x}}) \hbar/2M\omega}{\left\{ E - 2\hbar\omega - \frac{\hbar^2}{2m} (\hat{\lambda} + \hat{\mathbf{k}} + \hat{\mathbf{x}})^2 \right\} \left\{ E - \hbar\omega - \frac{(\hat{\lambda} + \hat{\mathbf{k}})^2}{2m} - \frac{\hbar}{2M\omega} \sum_{\hat{\mathbf{x}}} \frac{g^2(\hat{\mathbf{x}})}{E - 2\hbar\omega - \frac{\hbar^2}{2m} (\hat{\lambda} + \hat{\mathbf{k}} + \hat{\mathbf{x}})^2} \right\}} \quad (41)$$

4. Effective Mass for One-Dimensional Problem

In order to discuss the effects of two and three quantum contributions and to estimate the effective masses for the strong interactions occurring in ionic crystals, it is convenient first to discuss a certain one-dimensional case where the integrals occurring are easier to evaluate than for three-dimensional. One can show that the one-dimensional integrals are certain averages over the integrands of three-dimensional integrals and differ from the latter by factors of the order of unity. We shall compare the F.P.Z. solution with the more complete solution for different strengths of interaction. At weak interactions ($\beta^2 \pi < 1$) we find that the two quantum terms give a small

32) W. Schmeidler, "Integralgleichungen," Akademische Verlag, Leipzig, 1950, p. 270.

correction in energy to the F. P. Z. solution and that inclusion of three quantum terms gives an additional negligible correction. For stronger interactions ($\beta^2 \pi \approx 2$) the two-quantum solution yields appreciable corrections to the energy and effective mass, and the three-quantum terms give small corrections. For $\beta^2 \pi > 3$ it would be necessary to include more quanta in order to obtain adequate results. It appears, though, that the expression $E_0 = -\beta^2 \pi \hbar \omega$ suggested by intermediate coupling theory is a good approximation for the range of interactions $\beta^2 \pi < 3$, while the effective mass $m^* = m_c (1 + \beta^2 \pi / 2)$ is less than the true value.

We shall study the problem where $g(k) = \frac{g}{L^{1/2}}$ = constant in which L is the length of the quantization box. For the one-dimensional problem

$$\sum_k (\dots) \rightarrow \int \frac{L(\dots) dk}{2\pi}.$$

If one introduces dimensionless units by measuring energy in terms of $\hbar \omega$ and momentum in units of $(2m\hbar\omega)^{1/2}$, the measure of coupling strength becomes $\beta^2 \pi$ where

$$\beta^2 \pi = \frac{1}{2} \frac{1}{(\hbar\omega)^2} g^2 \left(\frac{\hbar}{2M\omega} \right) \left(\frac{2m\omega}{\hbar} \right)^{1/2}. \quad (42)$$

In addition, the quantity

$$B = \frac{-\hbar}{2M\omega} \sum_x \frac{g^2(x)}{E - 2\hbar\omega - \frac{\hbar^2}{2m} (\lambda + k + x)^2} \quad (43)$$

has the dimensions of energy, and in dimensionless units $B = \frac{\beta^2 \pi}{\sqrt{2-E}}$.

The Fock equations including three-quantum terms become

$$\{E - \lambda^2\} \chi_0 = \bar{p} \int_{-\infty}^{+\infty} \sum_1^{\prime} (k) dk$$

$$\begin{aligned} \left\{ E - 1 - (\lambda + k)^2 \right\} \zeta_1'(k_1) &= \beta X_0 + \sqrt{2} \beta \int_{-\infty}^{+\infty} \zeta_2'(k_1 k_2) dk_2 \\ \left\{ E - 2 - (\lambda + k_1 + k_2)^2 \right\} \zeta_2'(k_1 k_2) &= \frac{\beta}{\sqrt{2}} \left\{ \zeta_1'(k_1) + \zeta_1'(k_2) \right\} \\ &+ \sqrt{3} \beta \int_{-\infty}^{+\infty} \zeta_3'(k_1 k_2 k_3) dk_3 \end{aligned} \quad (44)$$

$$\begin{aligned} \left\{ E - 3 - (\lambda + k_1 + k_2 + k_3)^2 \right\} \zeta_3'(k_1 k_2 k_3) &= \frac{\beta}{\sqrt{3}} \left\{ \zeta_2'(k_1 k_2) \right. \\ &+ \zeta_1'(k_2 k_3) + \zeta_2'(k_3 k_1) \left. \right\} . \end{aligned}$$

We have introduced the amplitudes $\zeta_1' = \frac{L^{1/2}}{(2\pi)^{1/2}} \zeta_1$, $\zeta_2' = \frac{L}{2\pi} \zeta_2$, etc.

Let us now discuss these equations according to the number of quanta. The one-quantum solution is

$$\left. \begin{aligned} \zeta_1'(k) &= \frac{\beta X_0}{E - 1 - (\lambda + k)^2} \\ \lambda^2 - E &= \frac{\beta^2 \pi}{\sqrt{1 - E}} \end{aligned} \right\} . \quad (45)$$

In Fig. 2 we plot $E(\lambda = 0) = E_0$ as a function of $\beta^2 \pi$. To find the mean velocity \bar{v} we must compute $\frac{\partial E^\dagger}{\partial \lambda}$

$$\bar{v} = \frac{2\lambda}{1 + \beta^2 \pi / 2(1 - E)^{3/2}} . \quad (46)$$

† It can be shown by methods similar to those in Ref. 30 that $\bar{v} = dE/d\lambda$ and $m^* = 1/d^2 E/d\lambda^2$. Compare, however, the elegant proof of Bogoliubov¹⁷⁾.

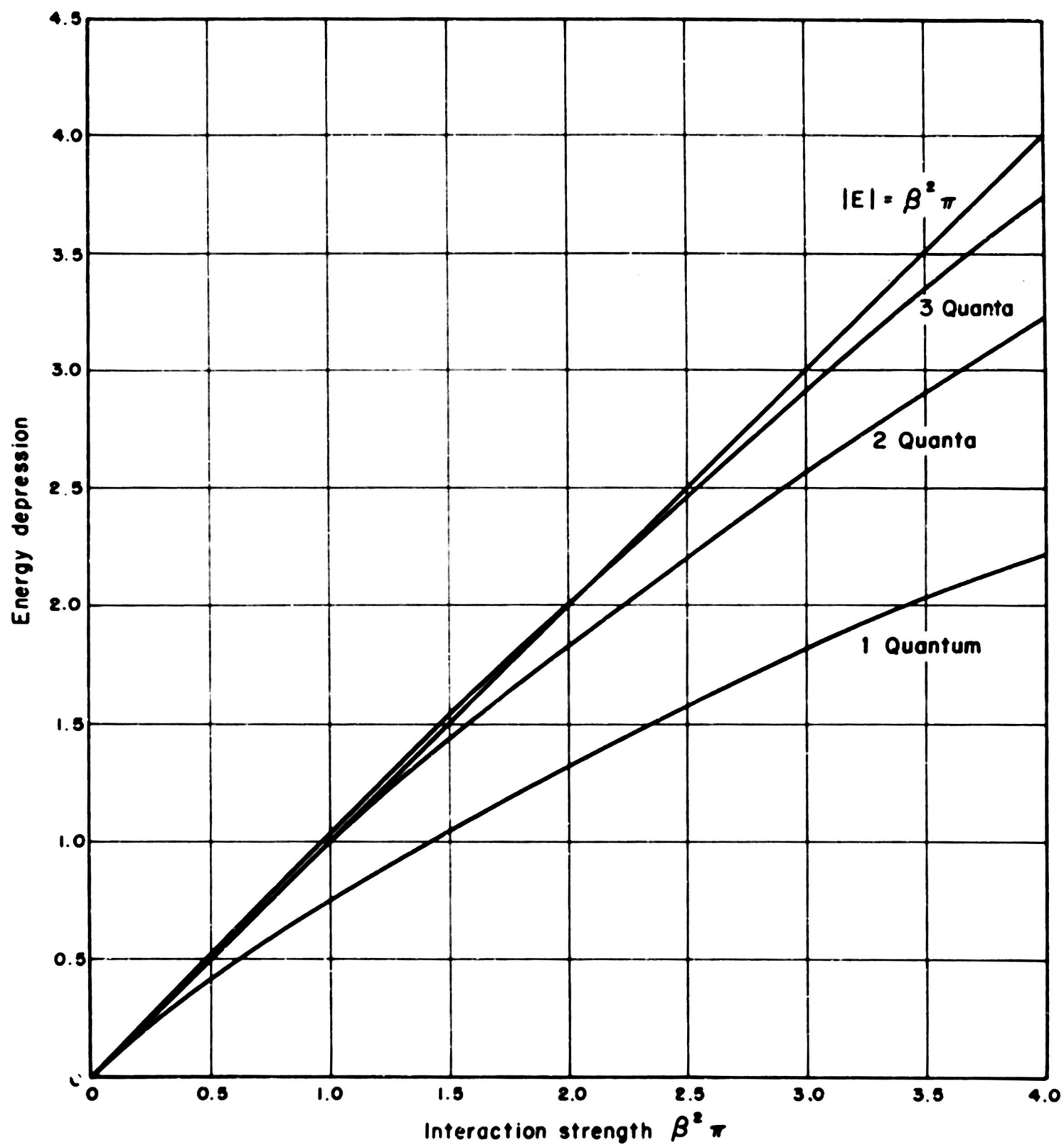


Fig. 2. Energy depression vs. interaction strength.

To find the effective mass for small values of the total momentum we set $E = E_0 + (\lambda^2/m^*)$ and expand to order λ^2 . Then

$$m^* = 1 + \frac{\beta^2 \pi/2}{(1 - E_0)^{3/2}} \quad (47)$$

This is plotted as a function of $\beta^2 \pi$ in Fig. 3; $m^* \rightarrow 1 + \frac{\beta^2 \pi}{2}$ as $\beta^2 \pi \rightarrow 0$ and $m^* \rightarrow 1.50$ as $\beta^2 \pi \rightarrow \infty$.

To find the two-quantum solution one must solve the pair of integral equations

$$\begin{aligned} \{E - \lambda^2\} \chi_0 &= \beta \int_{-\infty}^{+\infty} \zeta'(k) dk \\ \{E - 1 - (\lambda + k)^2 + B\} \zeta'(k) &= \beta \chi_0 + \beta^2 \int_{-\infty}^{+\infty} \frac{\zeta'(k') dk'}{E - 2 - (\lambda + k + k')^2} \end{aligned} \quad (48)$$

The Liouville-Neumann series is, with $B = \beta^2 \pi / \sqrt{2 - E}$ and the abbreviations $a = \sqrt{1 - E - B}$, $C = \sqrt{2 - E}$,

$$\begin{aligned} \zeta &= \frac{-\beta \chi_0}{a^2 + (\lambda + k)^2} \left\{ 1 + \beta^2 \int_{-\infty}^{+\infty} \frac{dk'}{\{a^2 + (\lambda + k')^2\} \{C^2 + (\lambda + k + k')^2\}} \right. \\ &\quad + \beta^4 \int_{-\infty}^{+\infty} \frac{dk'}{\{a^2 + (\lambda + k')^2\} \{C^2 + (\lambda + k + k')^2\}} \\ &\quad \left. + \beta^6 \int_{-\infty}^{+\infty} \frac{dk''}{\{a^2 + (\lambda + k')^2\} \{C^2 + (\lambda + k + k')^2\}} + \dots \right\} \end{aligned} \quad (49)$$

With the help of the integral

$$\int_{-\infty}^{+\infty} \frac{dk'}{(a^2 + k'^2)(C^2 + (k + k')^2)} = \frac{\pi \left(\frac{1}{a} + \frac{1}{C} \right)}{k^2 + (a + C)^2} \quad (50)$$

we obtain

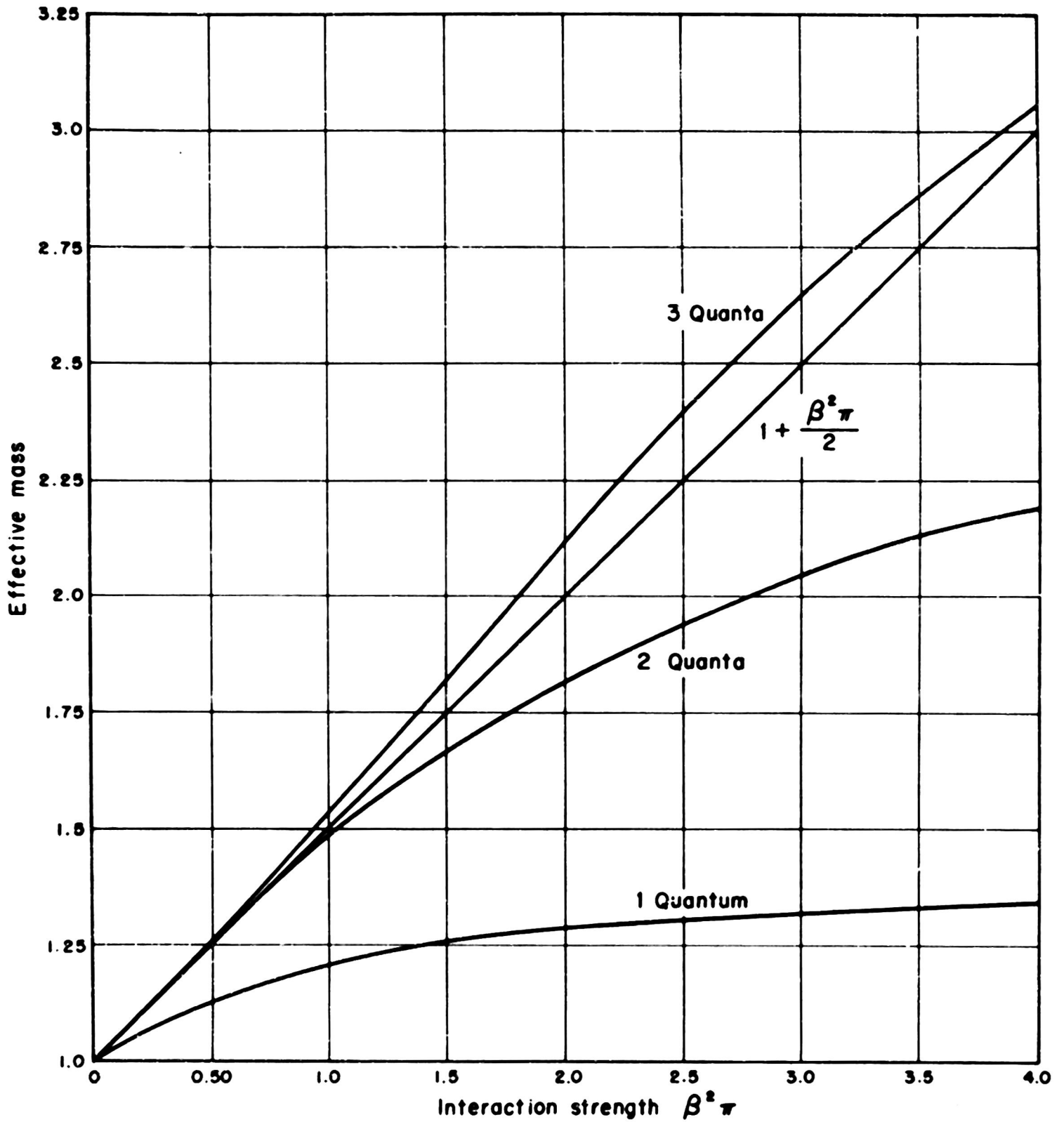


Fig.3. Effective mass vs. interaction strength.

$$\zeta = \frac{-\beta X_0}{(\lambda + k)^2 + a^2} \left\{ 1 + \beta^2 \pi \frac{\left(\frac{1}{a} + \frac{1}{C}\right)}{k^2 + (a + C)^2} + \beta^2 \pi \left(\frac{1}{a} + \frac{1}{C}\right) \beta^2 \right. \\ \left. \int_{-\infty}^{+\infty} \frac{dk'}{\left\{ (\lambda + k + k')^2 + C^2 \right\} \left\{ (\lambda + k)^2 + a^2 \right\} \left\{ k'^2 + (a + C)^2 \right\}} + \dots \right\} \quad (51)$$

$$\lambda^2 - E = \frac{\beta^2 \pi}{a} + (\beta^2 \pi)^2 \frac{\left(\frac{1}{a} + \frac{1}{C}\right) \left(\frac{1}{a + C} + \frac{1}{a}\right)}{\lambda^2 + (C + 2a)^2} + (\beta^2 \pi)^3 \left(\frac{1}{a} + \frac{1}{C}\right)^2 \frac{1}{2(a + C)} \\ \left\{ \frac{1}{(a + c)^2 [\lambda^2 + (2a + C)^2]} + \frac{2(2a + C) \left(\frac{1}{a + C} + \frac{1}{a}\right)}{[\lambda^2 + (2a + C)^2]^2} \right\} + \dots \quad (52)$$

In order to evaluate the next term one must compute the three-denominator integral. This is easy to do but will not be written here. For the one-dimensional problem the kernel is

$$K(x, \xi) = \frac{1}{\left\{ (\lambda + x + \xi)^2 + C^2 \right\}} \cdot \frac{1}{\left\{ (\lambda + \xi)^2 + a^2 \right\}} \quad (53)$$

and the convergence condition is $\beta^4 \pi^2 \leq 4 C^3 a^3$. Proceeding as in the one-quantum case, we find for the effective mass

$$m^* = 1 + \frac{\beta^2 \pi}{4a_0^3} \left\{ 2 + \frac{\beta^2 \pi}{C_0^3} \right\} + \frac{(\beta^2 \pi)^2}{2(2a_0 + C_0)} \left\{ \frac{1}{a_0^2 C_0^3} + \frac{1}{C_0 a_0^4} \left(2 + \frac{\beta^2 \pi}{C_0^3} \right) \right\} \\ + \frac{(\beta^2 \pi)^2}{2a_0^2 C_0 (2a_0 + C_0)^2} \left\{ \frac{1}{C_0} + \frac{1}{a} \left(2 + \frac{\beta^2 \pi}{C_0^3} \right) + \frac{2}{2a_0 + C_0} \right\} + \dots \quad (54)$$

The results of the calculations for the two-quantum case are plotted in Figs. 2 and 3. It is seen that the two-quantum correction to the energy becomes appreciable for $\beta^2 \pi > 1$, while the correction to the effective mass is important for $\beta^2 \pi > 0.3$. For the higher values of $\beta^2 \pi$ it is necessary to in-

clude several higher terms in the series (Eq. 52). For example, for $\beta^2 \pi = 2$ the energy is $E_0 = -1.82$ and is divided as $-(1.51 + 0.25 + 0.05 + 0.01)$. Even for small values of $\beta^2 \pi$ it is important to include higher terms for large values of λ . It is interesting to note from Eq. (48b) that the onset of the continuum is depressed to an energy determined by $1 - E - B = 0$. This is illustrated in Fig. 4 where we plot the energy vs. momentum for $\beta^2 \pi = 1$. For higher λ the effective mass appears to be large. It is not clear how higher quanta will modify this effect.

In order to estimate the energy when the wave function includes three quantum contributions it is necessary to eliminate ζ_3 and to obtain an integral equation for ζ_2 . One finds

$$\left\{ E - 2 - (\lambda + k_1 + k_2)^2 + A \right\} \zeta_2'(k_1 k_2) = \frac{\beta}{\sqrt{2}} \left\{ \zeta_1'(k_1) + \zeta_1'(k_2) \right\} + \beta^2 \int \frac{\zeta_2'(k_2 k_3) + \zeta_2'(k_3 k_1)}{E - 3 - (\lambda + k_1 + k_2 + k_3)^2} dk_3, \quad (55)$$

$$\text{where } A = \frac{\beta^2 \pi}{\sqrt{3 - E}}.$$

In addition, we have the first two equations of set (44). We can no longer find a single integral equation which can be solved by iteration and whose convergence can be demonstrated. The procedure will be less systematic. We first drop the integral terms above and find for $\zeta_2'(k_1 k_2)$

$$\zeta_2' = \frac{\beta}{\sqrt{2}} \frac{\left\{ \zeta_1'(k_1) + \zeta_1'(k_2) \right\}}{\left\{ E - 2 - (\lambda + k_1 + k_2)^2 + A \right\}}. \quad (56)$$

This expression differs from the previous one only by the presence of the constant A. The wave functions and energy levels can therefore be found from Eqs. (51) and (52) by replacing a and C by

$$a' = \sqrt{1 - E - D}, \quad C' = \sqrt{2 - E - A}, \quad (57)$$

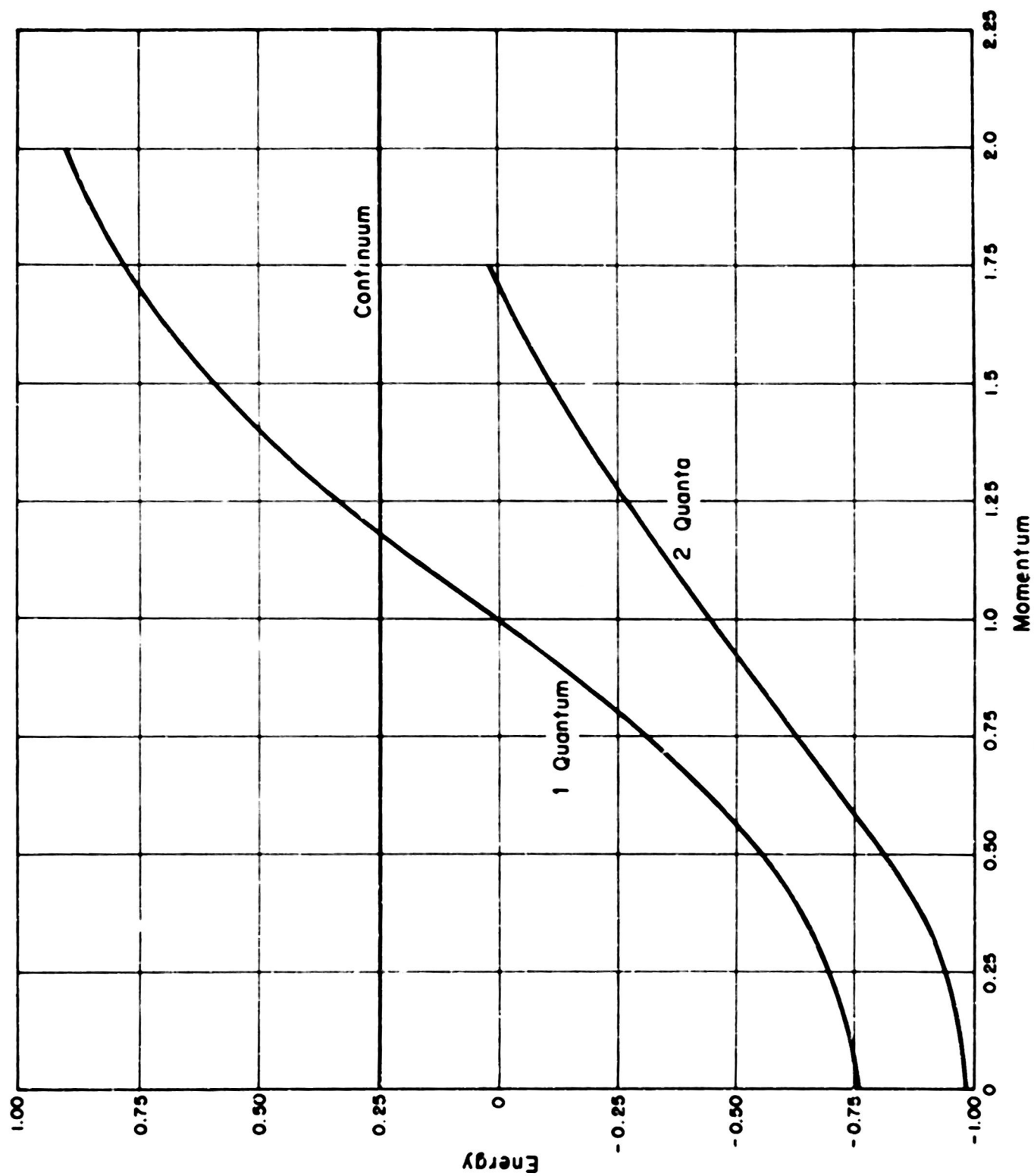


Fig. 4. Energy vs. momentum for $\beta^2 \pi = 1$.

where

$$D = \frac{\beta^2 \pi}{\sqrt{2 - E - A}}$$

The next correction may be found by inserting the $\zeta_2'(k_1 k_2)$ found, into the integral in Eq.(55). We find

$$\delta \zeta_2'(k_1 k_2) = \frac{\beta^2}{\lambda(k_1 + k_2)^2 + C'^2} \int_{-\infty}^{+\infty} \frac{\zeta_2'(k_2 k_3) + \zeta_2'(k_3 k_1)}{3 - E + (k_1 + k_2 + k_3 + \lambda)^2} dk_3. \quad (58)$$

Since $\zeta_2'(k_1 k_2)$ can be expressed explicitly in terms of $k_1 k_2$ and χ_0 this integral can be evaluated. Then inserting $\delta \zeta_2'$ into Eqs. (44a) and (44b), we find a correction to the energy of

$$\sqrt{2} \beta^4 \int_{-\infty}^{+\infty} \frac{dk_1}{E - 1 - (\lambda + k_1)^2} \int_{-\infty}^{+\infty} \frac{dk_2}{(\lambda + k_1 + k_2)^2 + C'^2} \int_{-\infty}^{+\infty} dk_3 \frac{\zeta_2'(k_2 k_3) + \zeta_2'(k_3 k_1)}{3 - E + (\lambda + k_1 + k_2 + k_3)^2} dk_3, \quad (59)$$

where

$$\zeta_2'(k_1 k_2) = -\frac{\beta}{\sqrt{2}} \frac{(\zeta_1'(k_1) + \zeta_1'(k_2))}{2 - E + (\lambda + k_1 + k_2)^2 - A}$$

and ζ_1' may be obtained from Eq.(51). Higher order corrections are obtained by iteration. From Figs. 2 and 3 we see that three-quantum effects influence the energy and effective mass to an important extent for $\beta^2 \pi > 3$. The effective mass is particularly sensitive to the number of quanta included and for $\beta^2 \pi > 3$ it is possible that the method of including a limited number of quanta breaks down. The calculations of Fig. 3 seem to point to a breakdown

of the linear dependence of m^* on $\beta^2 \pi$ for $\beta^2 \pi > 3$.

5. Three-Dimensional Case

Let us now examine the actual three-dimensional case. We introduce dimensionless units by measuring energy in units of $\hbar\omega$ and momentum in units of $\sqrt{2m\hbar\omega}$ so that the relation $E = \lambda^2/2m$ for a free particle goes over to $E = \lambda^2$. We make use of the fact that $\sum_{\underline{k}} \rightarrow \frac{V}{(2\pi)^3} \int k^2 dk d\Omega$. Then with

$$a = \frac{1}{2} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \frac{e^2}{\hbar\omega} \left(\frac{2m\omega}{\hbar} \right)^{1/2}$$

the equation for the energy, including two quantum terms, becomes

$$\left\{ \lambda^2 - E \right\} = \frac{a}{2\pi^2} \iiint \frac{dk d\Omega}{\left\{ (\underline{\lambda} + \underline{k})^2 + 1 - E - B \right\}} \left\{ 1 + \frac{a}{2\pi^2} \iiint \frac{dk' d\Omega'}{\left\{ (\underline{\lambda} + \underline{k} + \underline{k}')^2 + 2 - E \right\} \left\{ (\underline{\lambda} + \underline{k}')^2 + 1 - E - B \right\}} + \dots \right\}, \quad (60)$$

where

$$B(\underline{k}, \underline{\lambda}) = \frac{a}{|\underline{\lambda} + \underline{k}|} \sin^{-1} \left(\frac{|\underline{\lambda} + \underline{k}|}{\sqrt{2 + (\underline{\lambda} + \underline{k})^2 - E}} \right). \quad (61)$$

Neglecting the two-quantum contributions one finds the one-quantum expression

$$\lambda^2 - E = \frac{a}{\lambda} \sin^{-1} \frac{\lambda}{\sqrt{1 + \lambda^2 - E}}. \quad (62)$$

The lowest energy level is obtained for $\lambda = 0$ when $-E_0 = a/\sqrt{1 - E_0}$. This is the same expression that we had in the one-dimensional case provided we identify the $\beta^2 \pi$ used there with the a used here. One can obtain the effective mass by writing $E = E_0 + \lambda^2/m^*$ and developing in powers of λ . We find

$$m^* = \left(1 + \frac{a}{2} \frac{1}{(1 - E_0)^{3/2}}\right) / \left(1 + \frac{a}{3} \frac{1}{(1 - E_0)^{3/2}}\right). \quad (63)$$

The energy E_0 is plotted as a function of a in Fig. 3. In the limit of vanishing a one finds $m^* \rightarrow 1 + a/6$ so that the correction is $1/3$ that for the one-dimensional case. For very large a , $E_0 \rightarrow a^{2/3}$ and $m^* \rightarrow 1.13$.

Let us now turn our attention to the two-quantum contributions. The results of the one-dimensional case indicate that for actual crystals a two-quantum solution will not be adequate. Since the calculations are involved, we shall restrict ourselves to a discussion of the energy for $\lambda = 0$ as a function of interaction strength. The results for the energy are similar to those for the one-dimensional case. For the effective mass we would expect approximate agreement with the law $m^* = m_c(1 + a/6)$.

We notice that, because of the presence of the term $B(\vec{k})$ in the denominators, one does not have straightforward integrals. Consider the denominator $k^2 + 1 - E - B$ with $B = a/k \sin^{-1} k/\sqrt{2 + k^2 - E}$. For $k = 0$, $B \rightarrow a/\sqrt{2 - E}$, while for large k , $B \rightarrow 0$. It can be shown that assuming $B = \text{const.} = a/\sqrt{2 - E}$ introduces errors of the order 1 percent in the energy. In addition, a better constant value for B may be determined after one has approximate values for E . Thus the first term in the Liouville-Neumann series gives

$$\lambda^2 - E = \frac{a}{\lambda} \sin^{-1} \frac{\lambda}{\sqrt{1 + \lambda^2 - E - B}} \quad (64)$$

In order to compute the second term in the series, one must evaluate an integral of type

$$I = \iiint \frac{dk d\Omega}{\{(k)^2 + a^2\}} \iiint \frac{dk' d\Omega'}{\{(k + k')^2 + b^2\} \{(k')^2 + a^2\}}, \quad (65)$$

where we have put $a^2 = 1 - E - B$, $b^2 = 2 - E$. We write I in the form

$$I = \iiint \frac{d\vec{k} \, d\vec{k}'}{(k^2 + a^2) \{ (k - k')^2 + b^2 \} (k'^2 + a^2) k^2 k'^2} \quad .$$

and consider first

$$J = \iiint \frac{d\vec{k}'}{k'^2 (k'^2 + a^2) ((\vec{k} - \vec{k}')^2 + b^2)} = \int \theta(\vec{k}') \phi(\vec{k} - \vec{k}') d\vec{k}',$$

where

$$\theta(\vec{k}') = \frac{1}{k'^2 (k'^2 + a^2)} \quad ; \quad \phi(\vec{k} - \vec{k}') = \frac{1}{(\vec{k} - \vec{k}')^2 + b^2} \quad .$$

We now make use of the theorem

$$\int \Theta(\vec{\rho}) \Phi(\vec{\rho}) e^{-i\vec{\rho} \cdot \vec{k}} d\vec{\rho} = \int \theta(\vec{k}') \phi(\vec{k} - \vec{k}') d\vec{k}' \quad ,$$

where

$$\Theta(\vec{\rho}) = \left(\frac{\pi}{2} \right)^{1/2} \frac{1}{a^2} \frac{1}{\rho} \left\{ 1 - e^{-\rho a} \right\}$$

is the Fourier transform of $\theta(k')$ and $\Phi(\vec{\rho}) = \sqrt{\pi/2} \, e^{-b\rho}/\rho$ is the Fourier transform of $\phi(k')$. We have

$$J = \iiint d\vec{\rho} \, e^{-i\vec{\rho} \cdot \vec{k}} \left(\frac{\pi}{2} \frac{1}{a^2} \right) \frac{e^{-\rho b}}{\rho^2} (1 - e^{-\rho a}) \quad .$$

Introducing the angle $\cos \theta$ between \vec{k} and $\vec{\rho}$, integrating over θ , and inserting in the expression for I , one finds

$$I = \frac{8\pi^3}{a^2} \int_0^\infty \frac{dk}{k^2 + a^2} \int_0^\infty d\rho \, e^{-\rho b} \frac{(1 - e^{-\rho a})}{\rho k} \sin k\rho \quad ,$$

and finally,

$$I = \frac{8\pi^3}{a^2} \int_0^\infty \frac{dk}{(k^2 + a^2)k} \left(\tan^{-1} \frac{k}{b} - \tan^{-1} \frac{k}{a+b} \right) \quad . \quad (66)$$

An expression for I can be obtained in the form of a series by writing

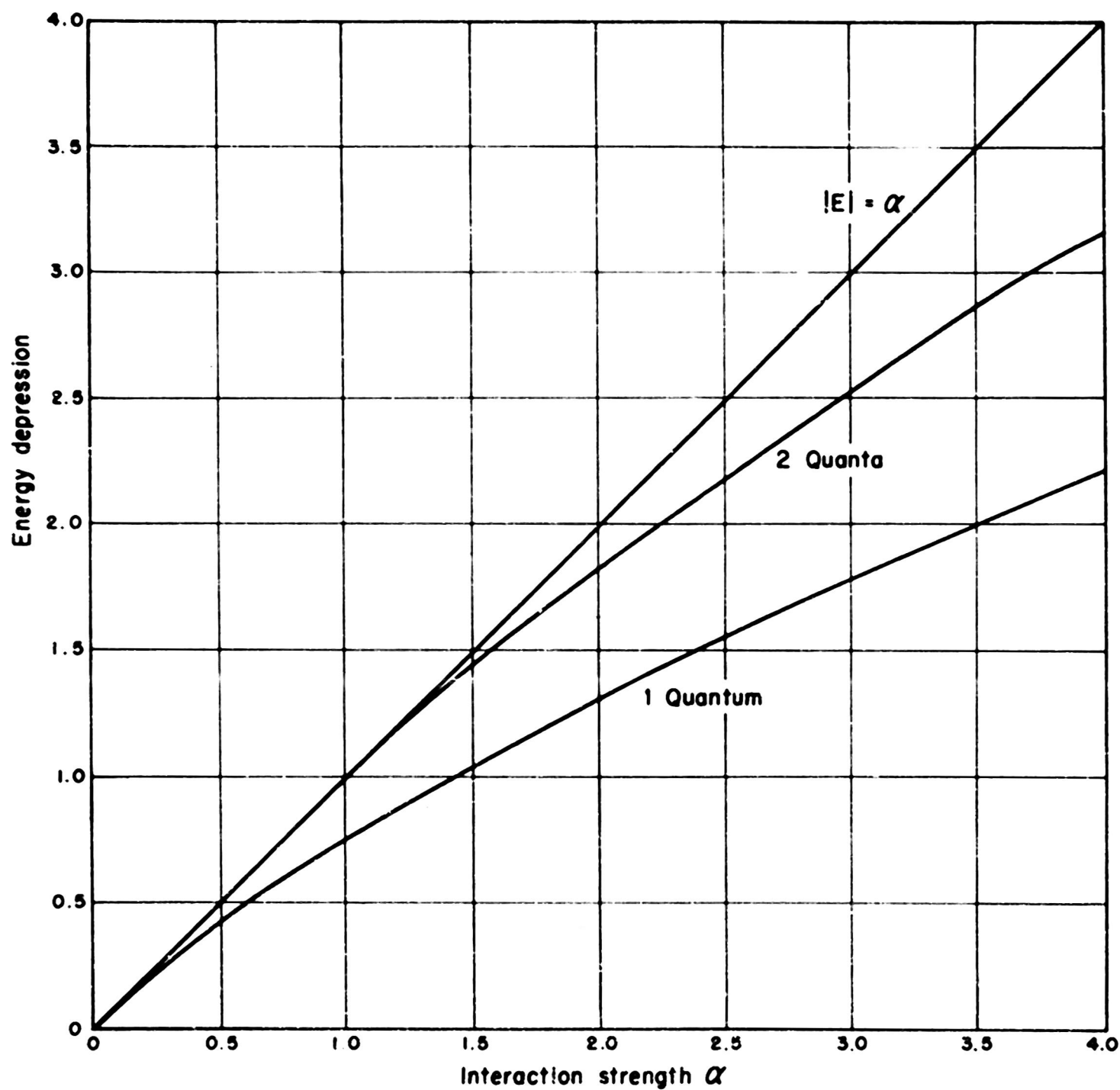


Fig. 5. Energy of lowest state (three dimensions).

$$\begin{aligned}\tan^{-1} x &= x - \frac{1}{3} x^3 + \frac{1}{5} x^5 - \dots & x^2 < 1 \\ &= \frac{\pi}{2} - \frac{1}{x} + \frac{1}{3x^3} - \frac{1}{5x^5} + \frac{1}{7x^7} - \dots & x^2 > 1\end{aligned}$$

Thus, to the second term, we find (for $\lambda = 0$) $-E = a/\sqrt{1-E-B} + I(a, b)$. The contributions of higher terms in the Liouville-Neumann series become progressively more difficult to evaluate. However, each term gives a positive contribution to the right-hand side of Eq.(60). Furthermore, one can over-estimate the contribution of each term by replacing the coupling denominator $(\hat{k} + \hat{k}')^2 + b^2$ by b^2 . Then each term is less than

$$\frac{a}{(2-E)} \frac{1}{\sqrt{1-E-B}}$$

times the previous one, and if one uses the overestimate, one obtains values of E which are too low. On the other hand, neglecting higher terms entirely gives values of E which are too high.

The results of the calculations of E vs. a are presented in Fig. 5. The behavior is very similar to that in one dimension.